Title: New Heteroatomic Polymer for More Efficient Solid
       Polymer Electrolytes for Lithium Batteries

Abstract

A new type of polymer is described that represents a new
composition of matter.  This polymer contains alternating
electronegative group III-VI elements connected with
hydrocarbon or fluorocarbon linkages to form a polyalkyl or
polyfluoroalkyl heteroatomic polymer.  These polymers can
be combined with lithium salts to form a solid polymer
electrolyte for use in electrochemical systems such as
batteries.  These new solid polymer electrolytes exhibit
lithium cation diffusion and lithium cation transport
numbers that are superior to similar solid polymer
electrolytes composed of polyethylene oxide.

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Description

SUMMARY OF THE INVENTION

Description of the Art


Improvements in solid state lithium batteries have
increasingly focused on the solid polymer electrolyte,
because this component continues to be the major obstacle in
fashioning solid state batteries that can displace their
liquid electrolyte counterpart.  Perfection of a successful
solid polymer electrolyte is the linchpin in obtaining a
competitive solid state lithium battery.

One of the primary objectives of recent SPE research has been to
improve the ionic conductivity of these materials.
Historically, this research has dealt with a number of
variations of the early poly(ethyleneoxide) [PEO] work of Armand
(Armand, M.B.; Chabango, J.M. and Duclot, M., 2nd Int. Conf on
Solid Electrolytes, Extended Abstracts 20-22, St. Andrews,
(**1978**))
in an attempt to find a polymer that could support good ambient
temperature ionic conductivity.  Early work involved making PEO
more amorphous by including flexible groups in the polymer.  Two
representative examples in this approach include poly[bis-

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(methoxyethoxyethoxide)]phosphazene MEEP and polyethoxy(ethoxy-ethoxy-vinyl)ether PEEVE (Blonsky; P.M., Shriver; D.R..; Austin; P. and Allcock; J., *J. Am. Chem. Soc.*, 106, 6854, (**1984**)). Inclusion of siloxane links in a PEO copolymer has been another general approach to enhance the amorphous character of PEO. Unfortunately, both approaches exhibit short comings including poor mechanical properties which limit their appeal. Recently, the combination of thermoplastic polymers with liquid electrolytes (i.e. ethylene carbonate, propylene carbonate) resulted in a"gelled" electrolyte and represented a clever attempt to tap the better properties of solvents in a solid electrolyte (Abraham, K. and Alamgir, G. *J. Power Sources*, 43-44, 195-208, (**1993**)). Although the ionic conductivities of the gelled polymer electrolytes have been among the highest measured in a room temperature polymer electrolyte, problems persist, because of the dubious mechanical and chemical properties of these materials (Dautenzenberg, G.; et al, *Chem. Mater.*, 6, 538-42, (**1994**)).

All of these approaches have focused on using ether oxygens in the "solvent" (either a liquid or a polymer) to solubilize and coordinate lithium salt cations that carry the ionic charge through the electrolyte. In the case of the liquid electrolyte, the solvent is carried along with the cation through the bulk of the electrolyte. In the case of the true "solventless" solid polymer electrolyte, the polymer is stationary and the cations are moved along the chain from one ether oxygen (active site) to the next by the segmental motion of the polymer. This is one reason why amorphous polymers are superior to crystalline polymers in promoting ionic conduction. The amorphous polymer model of cations moving along the chain is an oversimplification. Gray gives a more graphic description of the process that takes into account ion-ion association, and inter and intrachain ion hopping (Gray, F.M., "Polymer Electrolytes", RSC Monograph, The Royal Society of Chemistry, Cambridge, UK, (**1997**)). However, as Gray points out, the exact mechanism of ion conduction in a solventless polymer is as yet unknown.

In early attempts to improve on the properties of PEO, amorphous analogs such as poly(ethyleneimine) [-$(CH_2CH_2NH)_x$-, PEI] and polyalkylene sulfides [-($[CH_2CH_2]_nS)_x$-, PAS] were prepared and combined with various metal salts to form SPEs. These materials were intended to be the polymeric analogs to amino and thia organic solvents such as acetonitrile and dimethylsulfoxide that have been shown to form useful aprotic electrolytes

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for lithium batteries.  It was expected that the PEI and
PAS polymers would be more amorphous and would lead to more
conductive SPEs.  Unfortunately, this was not the case, and
both polymers were found to have properties that were, at
best, equivalent to PEO.  The instant invention is designed
to overcome the shortcomings of the solid polymer
electrolyte materials developed to date.

OBJECTS OF THE INVENTION

It is an object of the invention to provide the novel
compounds of formulas I and II and a process of preparing
the same.

It is another object of the invention to provide a novel
process for the preparation of solid polymer electrolytes
using polymer compounds of the formula I and various
lithium salts.

It is still another object of the invention to describe
novel uses of these new compounds.

These and other objects and advantages of the invention
will become obvious from the following detailed
description.

Summary of the Invention

The present invention constitutes a new family of polymers that
can be used for a variety of applications, including preparation
of solid polymer electrolytes for batteries.  The combination of
inorganic elements with organic carbon segments to form a
thermodynamically stable material is novel and heretofore
unprecedented.  The novelty of the proposed material lies in its
unique combination of soft acid, strong acid elements linked
together with organic spacers to provide a new material with an
amorphous character and physical and chemical properties
distinct from its counterparts polyethyleneoxide or
polyethyleneimine.

One general embodiment of the present invention can be
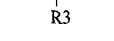summarized by the general structure shown below.

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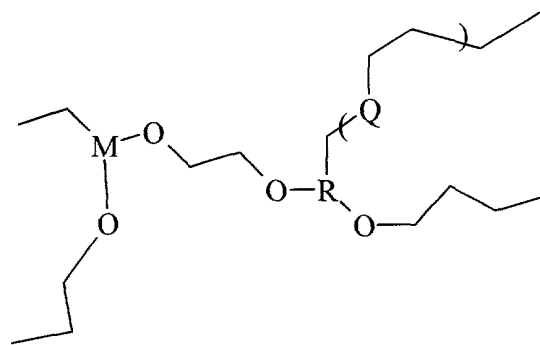
**Formula I**

Where R is an element chosen from the group P or B or Al
and M is an element chosen from the group Si or Ti and Q is
an element chosen from the group S, O or N. The phosphorus
can be present in either the $^+3$ or $^+5$ oxidation state

especially  These elements are connected using
hydrocarbon or fluorocarbon spacers, an example of which is
the $-CH_2-CH_2-$ ethylene linkage, and the entire molecule
forms a heteroatomic polymer. The polymer can be of
varying molecular weight ranging from 400 to 1,000,000 MW.
The array of ethylene spacer and element groups , i.e.

 can vary from an even distribution of each ethylene
spacer and element group to an uneven distribution in
ratios of 2 Q1 groups to one Q2 group to 5 Q1 groups to 1
Q2 group. Besides using ethylene carbon spacers in this
polymer, the elements can also be connected using propylene
and butylenes spacers. In addition, combinations of
ethylene and propylene or butylene spacers can be used to
connect the heteroatomic elements in the polymer. The
spacers can also have alternating odd and even numbers of -
CH2- or
-CF2- links. This will ensure greater amorphous character
in the polymer. Fluorocarbon analogs to these hydrocarbon
groups can also be employed together with hydrocarbon
groups or in direct replacement for hydrocarbon groups. In
addition to using the select elements directly, in certain
circumstances some of these select elements can contain
organic substitutents that modify the characteristics of
the polymer. For example: in the case of P or N, an
organic substitutent can be added prior to polymerizing the

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monomers used to prepare the polymer $\overset{\wedge\underset{R3}{N}\wedge}{}$ In this
instance, the R3 group can be an alkyl or aryl group, e.g.
methyl, nitrophenyl or aminophenyl group.  The same
circumstances apply to the triavalent element phosphorus.
In this latter instance, the P atom could be connected to
ethylene groups via an oxygen atom, or could be bonded
directly to the carbon of the ethylene group or similar
alkyl or fluoroalkyl substituent or spacer.  Here again the

species with phosphorus in the $^+5$ $\overset{|}{\underset{}{P}}{\scriptstyle\searrow O}$ oxidation state are
also viable.


In another embodiment of the basic concept, of the
essentials of the invention could be combined according to
the following general structure:


$$\text{-}(\overset{\wedge}{}\text{R1}\overset{\prime\prime}{}\wedge\diagup\overset{\wedge}{}\text{R2}\overset{\prime\prime}{}\wedge)_n$$
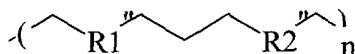
**Formula II**


Where R1 is an element chosen from the group N, B or S and R2 is
an element chosen from the group: O or P.  In addition, R1 can
be O while R2 is P in this compound.  In all cases, phosphorus
can be in the $^+3$ or $^+5$ oxidation state.  Once again, these
elements are connected using ethylene or propylene spacers and
the entire molecule forms a heteroatomic polymer.  The polymer
can be of varying molecular weight ranging from 400 to 1,000,000

MW.  The array of alkylene element groups , i.e. $(\overset{\wedge}{}\text{RI}\overset{\wedge}{})_n$ can vary
from an even distribution of each distribution of ethylene
element group to an uneven distribution in ratios of 2 R1 groups
to one R2 group to 5 R1 groups to 1 R2 group.  Besides using
ethylene carbon spacers in this polymer, the elements can also
be connected using propylene and butylene spacers.  In addition
combinations of ethylene and propylene or butylene spacers can
be used to connect the heteroatomic elements in the polymer.
These alkyl or fluoroalkyl spacers could be branched with alkyl
or fluoroalkyl side chains emanating from the backbone of the
spacer group.  In addition to using the select unsubstituted
elements directly, in certain circumstances some select elements
can contain substitutents to modify their chemical
characteristics and subsequently those of the polymer.  For

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example: in the case of P or N, an organic substitutent can be
added prior to polymerizing the monmers used to prepare the

polymer $\overset{\displaystyle \frown N \frown}{\underset{R3}{|}}$ In this instance, the R3 group can be a aromatic
or aliphatic in nature, e.g. methyl, phenyl, nitrophenyl or
aminophenyl group. The same circumstances apply to the
pentavalent form of phosphorus.
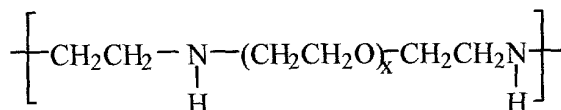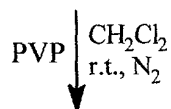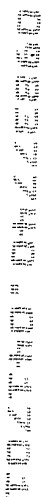
Examples of the Described Invention

The novel process of the invention for the preparation of a
compound of the formula II by reacting a compound such as ethyl
phosphite with ethylene glycol as described in the following
example. In the following examples, there are described several
preferred embodiments to illustrate the invention. However, it
should be understood that the invention is not intended to be
limited to the specific embodiments.

EXAMPLE 1

To prepare the oxyphosphorus polymer stoichiometric
quantities of ethylphosphite and ethyelene glycol are added
to anyhydrous methylene chloride with Nafion 117 pellets as
an acid catalyst. The solution mixture is then heated to
60°C and refluxed under dry agron gas for 10 hours to
effect the polymerization of the product. At the end of
this period, the methylene chloride is removed using a
rotary evaporator and the polymeric product is harvested,
and purified using mutiple extractions with drymethylene
chloride. The final product is dried overnight in a vacuum
oven at 40°C.
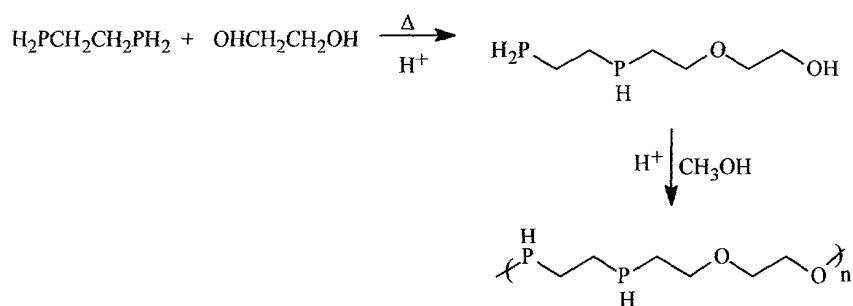


A similar procedure can be used to prepare polymers
containing N and O as depicted below:

$$Br-CH_2CH_2-Br \ + \ NH_2-(CH_2CH_2O)_x-CH_2CH_2NH_2$$

$$\xrightarrow[\text{r.t., } N_2]{\text{PVP} \ | \ CH_2Cl_2}$$

$$\left[ CH_2CH_2-\underset{H}{N}-(CH_2CH_2O)_x-CH_2CH_2\underset{H}{N} \right]$$


EXAMPLE 2

As an alternative, compounds of the general formula I can be prepared according to the following reaction scheme:

$$HO\left[\underset{CH_3}{\overset{}{Si}}\diagdown O\right]_n H \ + \ Cl-\underset{\underset{Cl}{|}}{\overset{\overset{O}{\|}}{P}}-Cl \ + \ HO\left[CH_2CH_2\right]_x \diagup O\diagdown H$$

$$\xrightarrow[\text{Base}]{\text{Toluene} \quad | \quad \text{Lithium Salt}}$$
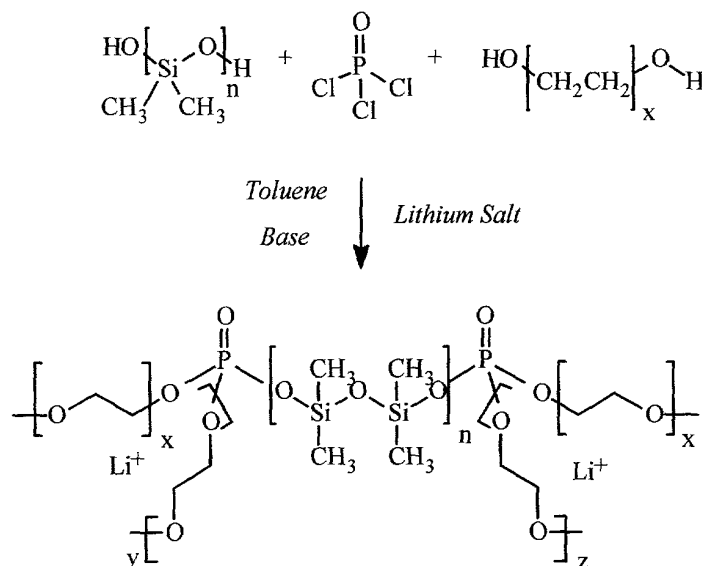


In this instance, stochiometric quantities of hydroxydimethylsiloxane is combined with trichlorophosphite and ethylene glycol in toluene and the mixture is acidified using Nafion 117 pellets as an acid catalyst. The solution mixture is then heated to 60°C and refluxed under dry agron gas for 10 hours to effect the polymerization of the product. At the end of this period, the methylene chloride is removed using a rotary evaporator and the polymeric product is harvested, and purified using mutiple extractions with drymethylene chloride. The final product is dried overnight in a vacuum oven at 40°C.

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EXAMPLE 3

Using these polymers and salts of lithium, one can easily
prepare solid polymer electrolytes for use in lithium
batteries. In this manner, we have prepared a solid polymer
electrolyte composed of a P, O polymer and lithium perchlorate
($LiClO_4$) by dissolving the $LiClO_4$ in anhydrous ethanol and then
combining this solution with a 400MW P, O polymer in an 8:1
$Li^+$:O, P ratio. This resulted in a viscous, clear liquid. An
alternative approach is to dissolve the lithium salt and the
polymer in dry methanol and then remove the methanol using a
vacuum apparatus. The product is a clear film. Newer lithium
salts such as lithium bisfluoroethanesulfonylimide (BETI) or
lithium bisperfluoromethanesulfonylimide can also be used in
place of lithium perchlorate.


EXAMPLE 4

To demonstrate the utility of the proposed polymer in a solid
polymer electrolyte, we characterized the bulk conductivity
and ionic diffusion properties of polymer electrolytes
prepared using these new polymers at room temperature using a
Radiometer Model PGZ 301 electrochemical test analyzer
together with model 4 Voltamaster impedance software. A
polypropylene test cell fitted with two polished, stainless
steel blocking electrodes and a Sensotec model GM force gauge
together with a steel screw-type pressure holder completed the
test apparatus used for the impedance measurements.

Polymer/salt complexes were prepared using the new polymers
and $LiClO_4$. A second test SPE was prepared using the new
polymer and lithium trifluoromethane sulfonimide (LiIm). A
control SPE was prepared using $5 \times 10^5$ MW PEO and $LiClO_4$
(Aldrich Chemical Co.) according to the procedures of Weston &
Steele (Weston;J.E. and Steele; B.C.H., *Solid State Ionics*, 7,
81-88, (**1982**)). All test were conducted in a dry glove box at
room temperature. The conductivity of the electrolyte was
determined by taking the reciprocal of the bulk resistance
($R_b$) at the intercept of the real axis (Z') of the Nyquist
plots. In keeping with literature reports Fritz, and Khun, *J.
Power Sources*, 41, 253-261, (**1993**) and Capuano, F.; Croce, F.
and Scrosati, B., *J. Electrochem. Soc.* 138, (7), 1918-1922,
(**1991**)), we acquired impedance spectra for each SPE in the
range from 100kHz to $10^{-3}$Hz. In this manner, both the bulk
resistance ($R_b$) and diffusion impedance ($Z_d$) of the

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electrolyte can be determined. The cation transference number $t_+$, can then be calculated from the relationship:

$$t_+ = (Z_d/R_b+1)^{-1}$$

A number of experiments were completed to establish the $D_+$ and $t_+$ of the new polymer/$LiClO_4$ SPE and the PEO control for comparison with the computer simulation results for these materials.

In another series of experiments, the cation diffusion coefficient ($D_+$) was determined using a chronopotentiometric method described by Ma et al (Ma, Y.; Doyle, M.; Fuller, T.F.; Doeff, M.M.; DeJonghe, L.C. and Newman, J., *J. Electrochem Soc.*, 142, (6), 1859-68, (**1995**). These authors developed this technique to measure $D_+$ using LiTf in poly(ethylene oxide). We used 8:1 O:Li $LiClO_4$ in PEO as a control and 8:1 O:Li $LiClO_4$ in our new polymer as the test SPE.

In addition to EIS, we used the Isothermal Transient Ionic Current (ITIC) method of Watanabe et al (Watanabe, M; Rikukawa, M; Sanui, K. and Ogata, N., J. Appl Phys., 58, (2), 736-740, (**1985**)) as a second, independent method to determine the cation transport number ($t_+$) for $LiClO_4$ in polyoxyamine. Watanabe measured $t_+$ of LiSCN in poly(ethylene succinate). Fritz and Kuhn (Fritz, H.P. and Kuhn, A., J. Power Sources, 41, 253-61, (**1991**)), employed the same technique to measure the $t_+$ of $LiClO_4$ in propylene carbonate (PC). We employed our test cell to measure the $D_+$ of 1M $LiClO_4$ in PC and 8:1 O:Li $LiClO_4$ in our test polymer.

The diffusion coefficients results for our test polymer SPE and two control SPEs prepared using PEO are summarized in the following table.

**Table 1**
**Comparative Cation Diffusion Results for Various SPEs**

| Sample | $D_+$ $cm^2/sec$ |
|---|---|
| PEO/$LiClO_4$ | $9.1 \times 10^{-8}$ |
| PEO/LiTf* | $7.5 \times 10^{-8}$ |
| Test polymer/$LiClO_4$ | $6.7 \times 10^{-7}$ |

Ma, Y.; Doyle, M.; Fuller, T.F.; Doeff, M.M.; DeJonghe, L.C. and Newman, J., J. El;ectrochem Soc., 142, (6), 1859-68, (**1995**).

As can be seen from these results, our experimentally determined $D_+$ for the controls agree well with literature results.  As shown here, the $D_+$ for our test polymer SPE is nearly an order of magnitude greater than the $D_+$ for either PEO control.  This is especially noteworthy in light of the $D_+$ for LiTf which is known to dramatically improve the ionic conductivity of PEO SPEs.  These results suggest that our test polymer is preferentially promoting cation diffusion through the SPE.

Obtaining these results using $LiClO_4$ is remarkable considering the difficulty normally encountered in solubilizing this strong Lewis salt in polymers other than PEO.

The results of the ITIC EIS testing in which the cation transference number was obtained are presented in the next table.

**Table 2**
**Cation Transference Number Results for Various SPEs**

| Sample | ITIC $t_+$ | EIS $t_+$ | Literature $t_+$ |
|---|---|---|---|
| $LiClO_4$/PC | 0.43 | | 0.36* (1M) |
| $LiClO_4$/test polymer | 0.68 | 0.71 | |
| $LiClO_4$/PEO | | 0.16 | 0.25 |

*Ue, M, *J. Electrochem. Soc.*, <u>141</u>, (12), 3336-42, (**1994**).

As can be seen from these data, the $t_+$ results for our polymer in an SPE with $LiClO_4$ are significantly better than comparable controls using PEO.  Our test results with the controls compare favorably with literature reports and there is continuity in the results for our test polymer SPE using two different test techniques.  These results strongly suggest preferential cation transport in the test SPE.

Bulk conductivity results for the test SPE and a PEO control were obtained from the EIS data by extrapolating the impedance curve to the intersection with the real (Z') axis at high frequency, calculating the reciprocal of this value ($R_b$) and normalizing for the SPE thickness.  The ionic conductivity of these two SPEs was found to be $8.6 \times 10^{-3}$ S/cm for the test polymer/LiIm SPE and $1 \times 10^{-7}$ S/cm for the PEO/$LiClO_4$ SPE control.

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